

SYNTHESIS, CHARACTERIZATION AND OPTIMIZATION OF  
MAGNETIC NANOSTRUCTURES BY SOL-GEL TECHNIQUE AND  
APPLICATION IN WATER PURIFICATION

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## ABSTRACT

Tailored maghemite nanoparticles with improved thermo-physical properties have attracted vast interest in current years. The design and synthesis of these particles have generated innovative magnetic, optical and other physical properties that arise from quantum size effect and enhanced surface to volume ratio with huge application significance. Tailored magnetic nanoparticles are prepared either by wet chemical methods such as colloidal chemistry or by dry processes such as vapor deposition techniques. This PhD project, aimed to develop novel vanadium doped maghemite ( $\text{Fe}_{2-x}\text{V}_x\text{O}_3$ ) particles with novel properties of  $\sim 5$  nm and nanohybrids of maghemite size ranges from 13-15 nm decorated multiwalled carbon nanotubes (MWCNTs) by wet methods. Tailored maghemite – MWCNTs nanohybrid was later, applied in efficient Lead removal application from aqueous solutions. The synthesis involved a facile Sol-gel route, with control over the size, morphology and the magnetic properties. Tailored maghemite particles were synthesized from a metal precursors and MWCNTs in a single pot reactor assembly, with forced nucleation in slight basic medium at pH  $\sim 9$ , yields crystalline, pure phase and thermally stable particles and nanohybrids. The synthesized particles and nanohybrids were characterized for different physical properties; crystallinity, phase purity and transformations, morphology, hydrodynamic particle size, polydispersity, magnetic properties, surface area studies, elemental and oxidation states of iron and vanadium, thermal stability, colloidal stability, zeta potential values and elemental ratios of iron, oxygen and carbon in tailored maghemite – MWCNT nanohybrids. The comparative changes in structural, magnetic, surface area and colloidal properties of the nanoparticles were found significant for future applications in nano devices, magnetic coatings, magnetic separations and other applications. Tailored maghemite – MWCNT nanohybrids were applied for efficient removal of Lead from aqueous solutions in batches magnetically. Lead adsorption mechanism was studied with Kinetics rate, adsorption isotherms. The effects of pH, contact time, adsorbent dosage, and agitation speed on the Pb (II) removal were scrutinized. Repeated adsorption–desorption cycles were studied to investigate the prolonged use of nanohybrids. The maximum removal achieved was  $\sim 94$  % in less than 2 h in a pH range of 6–7, which is very good yield with respect to previous studies. A mathematical model (Minitab version 15) was studied to validate the experimental method for the removal of Lead.

## ABSTRAK

Nanopartikel maghemite disesuaikan dengan baik sifat termo-fizikal telah menarik minat yang besar dalam tahun-tahun semasa. Reka bentuk dan sintesis zarah ini telah menjana magnet, optik dan lain-lain ciri-ciri fizikal yang inovatif yang timbul daripada kesan saiz kuantum dan permukaan dipertingkatkan kepada nisbah jumlah permohonan dengan kepentingan yang besar. Nanopartikel magnetik disesuaikan disediakan sama ada dengan kaedah kimia basah seperti kimia koloid atau oleh proses kering seperti teknik pemendapan wap. Projek PhD, bertujuan untuk membangunkan vanadium novel maghemite didopkan ( $\text{Fe}_{2-x}\text{V}_x\text{O}_3$ ) zarah dengan ciri-ciri novel  $\sim 5$  nm dan nanohybrids saiz maghemite antara 13-15 nm dihiasi nanotube karbon multiwalled (MWCNTs) dengan kaedah basah. Maghemite disesuaikan - MWCNTs nanohybrid kemudiannya, digunakan dalam cekap Lead penyingkiran permohonan daripada penyelesaian berair. Sintesis melibatkan facile Sol-gel laluan, dengan kawalan ke atas saiz, morfologi dan sifat-sifat magnet. Zarah maghemite disesuaikan telah disintesis daripada prekursor logam dan MWCNTs dalam periuk pemasangan reaktor tunggal, dengan penukleusan terpaksa dalam medium asas sedikit pada pH  $\sim 9$ , hasil kristal, fasa tulen dan zarah nanohybrids dan haba stabil. Zarah disintesis dan nanohybrids telah disifatkan dengan sifat-sifat yang berbeza fizikal; penghabluran, kesucian dan perubahan fasa, morfologi, saiz zarah hidrodinamik, polydispersity, sifat magnet, kajian kawasan permukaan, unsur dan pengoksidaan besi dan vanadium, kestabilan terma, kestabilan koloid, zeta nilai-nilai yang berpotensi dan nisbah unsur besi, oksigen dan karbon dalam maghemite disesuaikan - nanohybrids MWCNT. Perubahan perbandingan struktur, magnet, kawasan permukaan dan sifat-sifat koloid nanopartikel didapati penting bagi aplikasi masa depan dalam peranti nano, lapisan magnet, pemisahan magnet dan aplikasi lain. Maghemite disesuaikan - nanohybrids MWCNT telah digunakan untuk penyingkiran cekap Lead daripada penyelesaian akueus dalam kumpulan magnet. Utama mekanisme penjerapan telah dikaji dengan kadar Kinetics, isoterma penjerapan. Kesan pH, masa sentuhan, dos bahan penjerap, dan kelajuan pergolakan di Pb (II) penyingkiran telah diteliti. Berulang kitaran penjerapan-desorption dikaji untuk menyiasat penggunaan berpanjangan nanohybrids. Penyingkiran maksimum dicapai adalah  $\sim 94\%$  dalam masa kurang daripada 2 jam dalam pelbagai pH 6-7, yang merupakan hasil yang sangat baik berkenaan dengan kajian sebelum ini. Model matematik (Minitab versi 15) telah dikaji untuk mengesahkan kaedah eksperimen bagi penyingkiran Lead.

## CONTENTS

	<b>Page</b>
<b>SUPERVISORS' DECLARATION</b>	ii
<b>STUDENT'S DECLARATION</b>	iii
<b>ACKNOWLEDGEMENTS</b>	v
<b>ABSTRACT</b>	vi
<b>ABSTRAK</b>	vii
<b>CONTENTS</b>	viii
<b>LIST OF TABLES</b>	xii
<b>LIST OF FIGURES</b>	xiii
<b>NOMENCLATURES</b>	xix
<b>LIST OF ABBREVIATIONS</b>	xxii

### CHAPTER I     INTRODUCTION

1.1	Introduction	1
1.2	Problem statement	2
1.3	Objectives	4
1.4	Scope	5
1.5	Research contribution	6
1.6	Summary of chapters	6

### CHAPTER II     LITERATURE SURVEY

2.1	Introduction	9
2.2	Techniques for magnetic nanoparticles synthesis	12
2.2.1	Liquid phase methods	13
2.2.2	Two- phase methods (microemulsion)	15
2.2.3	Sol-gel method	18
2.2.4	Gas / aerosol - phase methods	22

2.2.5	Polyols method	23
2.2.6	Hydrothermal reaction methods	26
2.2.7	Sonolysis	29
2.2.8	Microwave irradiation	30
2.3	Magnetism	34
2.3.1	Types of magnetism	34
2.3.2	Magnetic behavior of Iron oxides	38
2.3.3	Maghemite	39
2.4	Applications	40
2.5	Vanadium	44
2.6	Carbon nanotubes	46
2.6.1	Purity of CNTs	47
2.7	Nanocomposites	48
2.7.1	Types of nanocomposites	49
2.7.2	Functional Carbon nanotube (CNTs) nanocomposites	50
2.7.3	Potential Applications of CNT–Metal Nanocomposites	51
2.7.4	Adsorption	52
2.8	Mathematical modeling	53
2.8.1	Minitab	54
2.8.2	Data and File Management Capabilities	54
2.9	Summary	55

### **CHAPTER III MATERIALS AND METHODS**

3.1	Introduction	56
3.2	Materials	57
3.2.1	Apparatus	58
3.3	Sol-gel technique	59
3.4	Synthesis of maghemite (reference material)	60
3.4.1	Flow chart	61
3.5	Synthesis of vanadium doped maghemite	62
3.5.1	Flow chart	64
3.6	Synthesis of maghemite - MWCNT composites / nanohybrids	65

3.6.1	Lead adsorption studies	65
3.6.2	Lead desorption studies	66
3.6.3	Flow chart	67
3.7	Characterization and analytical techniques	68
3.7.1	X- ray diffraction technique	69
3.7.2	Spectroscopy techniques	71
3.7.3	Microscopy techniques	79
3.7.4	Thermal analysis	83
3.7.5	Magnetic studies	84
3.7.6	Brunauer-Emmet-Teller (BET) surface area technique	86
3.7.7	Zeta potential studies	88
3.8	Summary	90

## **CHAPTER IV RESULTS AND DISCUSSION**

4.1	Introduction	91
4.2	Comparative study of synthetic maghemite and vanadium doped maghemites at different vanadium concentrations	92
4.2.1	X-ray diffraction (XRD) studies	92
4.2.2	X-ray Photon spectroscopy (XPS) studies	96
4.2.3	Fourier transform infrared spectroscopy (FTIR) studies	98
4.2.4	Transform electron microscopy (TEM) studies	101
4.2.5	Magnetic (VSM) studies	103
4.2.6	Thermogravimetric (TGA) studies	105
4.2.7	Electrophoretic characterization	108
4.2.8	Surface area studies	111
4.3	Synthesis of maghemite embedded multiwalled carbon nanotubes (MWCNT) nanohybrids	114
4.3.1	X-ray diffraction (XRD) studies	114
4.3.2	Field emission scanning electron microscopy (FE-SEM) studies	116
4.3.3	Fourier transform infrared spectroscopy (FTIR) studies	117
4.3.4	Magnetic (VSM) studies	118

4.3.5	Thermogravimetric (TGA) studies	120
4.3.6	Energy Dispersive X-ray spectroscopy (EDX)	121
4.3.7	Surface area studies	123
4.3.8	Electrophoretic Characterization	124
4.4	Application of maghemite – MWCNT nanohybrids for efficient lead removal from aqueous solution	124
4.4.1	Adsorption Mechanism	124
4.4.2	Study of Kinetics Rate	126
4.4.3	Adsorption Isotherm	128
4.4.4	Desorption experiments	129
4.5	Results of batch experiment	129
4.5.1	Effect of pH	129
4.5.2	Effect of contact time	130
4.5.3	Effect of dosage of adsorbent	131
4.5.4	Effect of agitation speed	132
4.5.5	Regeneration and reusability	133
4.6	Summary	134

## **CHAPTER V MATHEMATICAL MODELING**

5.1	Introduction	136
5.2	Data analysis	137
5.3	Model results	138
5.4	Effect of variables as response surface and contour plots	140
5.4.1	Main effect and Interactions plots for Pb (II) removal	140
5.4.2	Three dimensional plots for Pb (II) removal	143
5.5	Summary	144

## **CHAPTER VI CONCLUSIONS AND RECOMMENDATIONS**

6.1	Introduction	145
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6.2	Conclusions	146
6.3	Recommendations for Future research	147
	References	149

## APPENDICES

A	Nucleation	176
B	Braggs Law and Scherrer equation	179

## LIST OF TABLES

Table No.	Title	Page
2.1	The iron oxides (Cornell and Schwertmann, 2003)	11
2.2	Magnetic properties of the iron oxides	38
2.3	Theoretical and experimentally measured properties of carbon Nanotubes.	46
3.1	List of chemicals	57
4.1	XRD lattice parameters and sizes of maghemite and $\text{Fe}_{2-x}\text{V}_x\text{O}_3$	93
4.2	Experiment Description : 5mole% Vanadium doped maghemite	99
4.3	Magnetic properties studied by VSM at room temperature	105
4.4	Electrophoretic study of maghemite and vanadium doped maghemites	109
4.5	Surface area, Pore volume and Pore size values of $\gamma\text{-Fe}_2\text{O}_3$ and $\text{Fe}_{2-x}\text{V}_x\text{O}_3$	112
4.6	Average weight and atomic percentages of elements found in EDX studies	122
4.7	Calculated sorption capacity/time (qt), rate constant (k) and correlation coefficient ( $r^2$ ) from pseudo second order equation	127
5.1	Estimated regression coefficients, t values and P values from the data of CCD Experiments	137



5.2	The 3-factor CCD matrix and the value of response function (%)	138
5.3	Analysis of variance (ANOVA) for fit of Pb (II) removal efficiency (%)	139
5.4	Experimental range and levels of independent process variables	141

## LIST OF FIGURES

Figure No.	Title	Page
2.1	Crystal structures of (a) hematite and (b) magnetite	12
2.2	A comparison of published work (up to date) on the synthesis of SPIONs by three different routes. Sources: Institute of Scientific Information	13
2.3	Schematic representation of nanoparticle synthesis in microemulsion (a) by mixing two microemulsions (b) by adding a reducing agent, and (c) by bubbling gas through the microemulsion (Salazar-Alvarez., 2004)	16
2.4	Magnetic nanoparticles prepared in solution by: (a) Coprecipitation (maghemite). (b) Polyols process (Fe-based alloy). (c) Microemulsions (maghemite) (Tartaj et al., 2003)	17
2.5	Scheme showing the reaction mechanism of magnetite particle formation from an aqueous iron (III) solution by addition of a base	19
2.6	Schematic presentation of Hydrolysis and condensation of molecular precursors result in a wet gel; densified <i>xerogel</i> ; an <i>ambigel</i> , followed by supercritical drying to ultra high porous <i>aerogel</i>	20
2.7	Experimental setup for flame synthesis of iron oxide nanoparticles (Morales et al., 2003)	24
2.8	TEM images (a) sample I and (b) Sample II with (c) HRTEM of a single magnetite nanoparticle (Cullity and Stock, 2001)	25

2.9	Schematic diagram of the apparatus used by Teja for hydrothermal method (Xu et al., 2008)	27
2.10	TEM images of iron oxide nanoparticles obtained in (a) Experiment S1 (100,000X) and (b) experiment S2 (140,000X) (Xu et al., 2008)	28
2.11	Flow chart of sonochemical synthesis of iron oxide (Suslick., 1998)	30
2.12	(a) SEM image of sonochemically prepared Y-Fe-O (b) TEM image and SAED pattern shows the aggregates of ~ 3 nm sized particles (Gedye et al., 1986)	30
2.13	TEM images of the $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> nanoparticles generated by microwave irradiation (Kijima et al., 2007)	32
2.14	Size of nanoparticles formed at 150–250 °C varying the initial iron (III) chloride concentrations using microwave-assisted synthesis (Parsons et al., 2009)	33
2.15	TEM micrograph of iron oxide nanoparticles synthesized at 100 °C, with 30 min of pulsed microwave irradiation (Parsons et al., 2009)	33
2.16	Variations in hysteresis curve of different types of magnetic materials	37
2.17	Typical configurations utilized in nano-bio materials applied to medical or biological problems (Salata, 2004)	41
2.18	A typical high-gradient magnetic separation facility	43
3.1	Reactor assembly for ferrite and composite synthesis	58
3.2	Sol-gel chemistry, molecular precursors are converted to nanometer-sized particles to develop materials with distinct properties	59
3.3	Schematic diagram for the synthesis of maghemite nanoparticles	61
3.4	Schematic diagram for the synthesis of vanadium doped maghemite nanoparticles	64
3.5	Schematic presentation of Maghemite-MWCNT nanocomposites	67
3.6	Schematic of X-ray Diffractometer.	69
3.7	The XRD patterns were recorded using an X-ray diffractometer	70

	(Rigaku Miniflex II, Japan) employing graphite monochromator and CuK $\alpha$ radiation ( $\lambda = 0.15406$ nm).	
3.8	Emission processes of characteristic 2p photoelectron	72
3.9	Schematic of a Photoelectron spectrometer	73
3.10	The FTIR spectra were recorded using an FTIR Spectrophotometer (Nicolet 5DX FT-IR, USA)	74
3.11	Schematic of a FTIR spectrometer	75
3.12	Schematic working of Energy Dispersive X-ray spectroscopy (EDX), incoming X-ray emits an inner shell electron, leaving an empty space filled by outer shell electron by releasing a photon	77
3.13	Analysis was made by using an Atomic absorption spectroscopy (AAS, AAAnalyst 400 USA)	78
3.14	Schematic of Atomic absorption spectrometer	79
3.15	Schematic of transmission electron microscope (TEM) and the optical path	80
3.16	Schematic of Field emission scanning electron microscope (FE-SEM) showing optical path of light	82
3.17	Schematic of Thermogravimetry technique: instrumentation and working	83
3.18	Thermogravimetric curves that exhibit decomposition starting temperature $T_i$ and finish temperature $T_f$ . (Yang Leng, 2008)	84
3.19	Schematic of a VSM. The signal in the pick-up coils is caused by the flux change produced by the moving magnetic sample	85
3.20	Surface Analysis (ASAP 2020, Micromeritics, USA)	87
3.21	Schematic of BET surface area studies: technique instrumentation and working	88
3.22	Schematic representation of zeta potential in a colloidal suspension	89
4.1	Comparison spectra of maghemite and vanadium doped maghemites at different mol percentages	92
4.2	Phase transformation of maghemite to hematite in Thermodiffraction studies	94

4.3	Phase transformation of 2 mol% vanadium doped maghemite to hematite and reduced vanadium oxides	95
4.4	Phase transformation of 5 mol% vanadium doped maghemite to hematite and reduced vanadium oxides	95
4.5	XPS spectra of the 2 mole% and 5mol% vanadium doped maghemite nanoparticles	96
4.6	XPS spectra: (a) $\text{Fe}^{3+}$ with characteristic satellite peak (b) V 2p and O1s peaks of $\text{Fe}_{1.9}\text{V}_{0.1}\text{O}_3$ (5 mol %)	97
4.7	FTIR spectra of the synthetic maghemite and respective (2,5, and 6) mol% vanadium doped maghemites	98
4.8	Comparative FTIR spectra of the synthetic maghemite and 5 mol% vanadium doped maghemite	100
4.9	TEM micrographs for Maghemite samples, showing spherical shapes at 50 nm scale	101
4.10	TEM micrographs for $\text{Fe}_{1.96}\text{V}_{0.04}\text{O}_3$ (2 mol%), showing spherical and well dispersed nanoparticles at 100 nm scale	102
4.11	TEM micrographs for $\text{Fe}_{1.9}\text{V}_{0.1}\text{O}_3$ (5 mol%) showing well dispersed and spherical nanoparticles at (a) 5 nm and (b) 50 nm scales	102
4.12	Particle size distribution of ( $\text{Fe}_{2-x}\text{V}_x\text{O}_3$ ) with deviation in sizes	103
4.13	Magnetization curves for maghemite and $\text{Fe}_{2-x}\text{V}_x\text{O}_3$	104
4.14	Magnetization curves of maghemite and vanadium doped maghemite nanoparticles (at $\pm 200$ Oe)	105
4.15	TG-DTG curves of the synthetic maghemite and $\text{Fe}_{2-x}\text{V}_x\text{O}_3$ (2, 5 & 6 mol%) samples under $\text{N}_2$	106
4.16	Comparative DTG curve of maghemite and 5 mol% vanadium doped maghemite, showing transformation of iron phases and vanadium decomposition	107
4.17	hydrodynamic particle sizes of respective nanoparticles	109
4.18	Polydispersity (PDI) values calculated as a function of pH	110
4.19	Zeta potential values at different pH: maghemite, 2mole% and 5 mole% vanadium doped samples	110

4.20	BET surface area plot for: maghemite and different mol% V doped maghemites	113
4.21	Nitrogen adsorption-desorption isotherms: maghemite and 5 mol% V doped maghemite	113
4.22	Comparative X-ray diffraction study of maghemite (red lined graph), uncoated MWCNTs (green lined graph) and maghemite-coated MWCNTs (black lined graph) where Mh: Maghemite	114
4.23	Thermodiffractometry study of maghemite – MWCNT nanohybrids Phase transformation is observed as characteristic peaks of hematite can be seen in the spectrum	115
4.24	FE-SEM images of maghemite – MWCNTs nanohybrids (a) at 100,000 magnifications (b) at 150,000 magnifications	116
4.25	FE-SEM images of same Figure as shown in Figure 4.24 but at highest magnification one can achieve at the operating FE-SEM microscope	117
4.26	FTIR Spectra of uncoated MWCNTs and Maghemite-coated MWCNTs	117
4.27	Magnetic behaviors of MWCNT/maghemite composite (a) no external magnetic field (b) external field is applied	119
4.28	Hysteresis loop of maghemite nanoparticles and maghemite – MWCNT nanohybrids	119
4.29	Magnetization curves of maghemite and maghemite – MWCNT nanohybrids (at $\pm 500$ Oe)	120
4.30	TG-DTG curves of raw MWCNTs purified MWCNTs and maghemite – MWCNT nanohybrid samples under $N_2$	121
4.31	EDX analysis of maghemite – MWCNT nanohybrids	122
4.32	Figure.xii: BET surface area plot for maghemite – MWCNT nanohybrids	123
4.33	Bar graph of Pb (II) species as a function of pH	125
4.34	Pseudo-second order sorption kinetics of Pb (II) on to	127

	MWCNT/maghemite composite at various initial concentrations	
4.35	Relationship between $q_{eq}$ and $C_{eq}$ , at pH = 7 and stirring speed =120rpm and time =12 hours	128
4.36	The effect of pH on the amount of Pb (II) removed by MWCNT/maghemite	130
4.37	The effect of contact time on the amount of Pb (II) removed by uncoated MWCNTs (Gupta et al., 2011) and the maghemite-coated MWCNTs (Lead concentration 25 ppm, Dosage of adsorbent 50 mg, pH 7 and agitation speed 150 rpm)	131
4.38	The effect of dosage on the amount of Pb (II) removed by MWCNT/maghemite	132
4.39	Effect of agitation speed on removal of Pb (II), pH = 7, contact time = 120 min, removal > 90%	133
4.40	Removal capacities on recycling maghemite – MWCNT	134
5.1	A Comparison between experimental values and predicted values of Pb (II) removal efficiency by CCD	139
5.2	Main effect plots of pH, dosage, contact time and agitation speed versus Pb (II) % removal	140
5.3	Interaction plots presenting different parameters with their relationships	142
5.4	The response surface and plot of Pb (II) removal efficiency (%) as a function of pH and adsorbate concentration (mg/L)	143
5.5	The response surface and plot of Pb (II) removal efficiency (%) as a function of Time (min) and Agitation speed( rpm)	144
A.1	Schematic illustrating change in volume free energy, surface free energy and a total free energy; as function of nucleus radius	177
B.2	Bragg's Law equation. The lower beam must travel the extra distance (AB + BC) to continue traveling parallel and adjacent to the top beam	180

## NOMENCLATURES

### List of Symbols

Symbol	Meaning
K	Kelvin
°C	Degree Celsius
T <sub>N</sub>	Neel Temperature
K/s	Cooling rate
X <sub>M</sub>	Magnetic susceptibility
C <sub>M</sub>	Curie constant
T <sub>C</sub>	Curie Temperature
hν	photon energy
T	Absolute temperature (K)
T <sub>B</sub>	Blocking temperature
eg	Unpaired electrons
K <sub>eff</sub>	Anisotropy constant
E <sub>k</sub>	Kinetic energy
B.E	Binding energy
Pa	Pascal
T <sub>i</sub>	Lowest temperature when mass change is detected (TGA)
T <sub>f</sub>	Lowest temperature when the mass change is completed
V	Voltage (emf)
n	Turns of cross-sectional area
B	flux
M	Magnetization
H <sub>0</sub>	Measuring field

VT	Potential energy function
VS	Potential energy due to the solvent
VA	Potential energy due to attractive forces
VR	Potential due to repulsive forces
A	Hamaker constant
D	Particle separation
a	Particle radius
d	diffractional spacings
$a^0$	Lattice parameters
eV	Electron volt
Ms	Magnetic saturation
Oe	Oersted
Mr	Magnetic remanence
r <sup>2</sup>	correlation coefficients
pH <sub>iep</sub>	pH of zero potential
P/P <sub>o</sub>	Relative pressure
k	Rate constant of sorption (g/mgh-l)
q <sub>eq</sub>	Amount of Pb (II) ions adsorbed at equilibrium (mg/g)
C <sub>e</sub>	Equilibrium Lead ions concentration in solution (mg/L)
q <sub>max</sub>	Maximum capacity of adsorbent (mg/g)
K	Langmuir adsorption constant(L/mg)
xi	The factor
b <sub>0</sub>	The constant
b <sub>i</sub>	is the linear effect of the factor xi
b <sub>ii</sub>	Quadratic effect of the factor xi



$b_{ij}$	The interaction effects between the input factors $x_i$ and $x_j$
$R^2$	Coefficient of determination
$B_{hf}$	Magnetic hyperfine field
$q_t$	The amount of Pb (II) ions adsorbed at any time (mg/g)
$y$	The response

### Greek Symbols

Symbol	Meaning
	height of the energy barrier
$\lambda$	Wavelength
$\Phi$	Work function of spectrophotometer
$\delta$	Path difference
$\omega$	Frequency domain
$\nu$	Frequency
$\pi$	Solvent permeability
$\kappa$	Function of the ionic composition
$\zeta$	Zeta potential
$\theta$	Angle
$\varepsilon$	The residual term.

## LIST OF ABBREVIATIONS

MWCNTs	Multiwalled carbon nanotubes
nm	Nanometer
Pb	Lead
PDI	Polydispersity
HGMS	High gradient magnetic separations
CNTs	Carbon nanotubes
PEGPEI	Poly (ethylene imine) -g-poly (ethylene glycol)
ANOVA	Analysis of Variance
FTIR	Fourier transform infrared spectroscopy
AOT	Aerosol-OT anionic Surfactant
TEM	Transform electron microscope
RM	Reverse microemulsion
NaDDBS	Sodium benzene sulfonate
TEOS	Tetraethoxysilane
3D	Three dimensional
FKSSA	Faculty of Chemical Engineering & Natural Resource
IP	Isopropoxide
HRTEM	High-resolution transmission electron microscopy
SPIONs	Superparamagnetic iron oxide nanoparticles
PEG	Polyethylene glycol
PVP	Polyvinyl pyrrolidone
PEI	Poly ethylene imine
CTAB	cetyl tri methyl ammonium bromide
SWNT	Single walled nanotube
VSM	Vibrating sample magnetometer
TGA	Thermo-gravimetric analysis

BET	Brunauer-Emmet-Teller
PBS	Poly butylene succinate
EDX	Energy Dispersive X-ray spectroscopy
XRD	X-ray diffraction
AAS	Atomic absorption spectroscopy
XPS	X-ray photon spectroscopy
AES	Auger electron spectroscopy
DTA	Differential thermal analysis
SEM	scanning electron microscope
FFT	Fast Fourier transform
DVLO	Derjaguin, Verwey, Landau and Overbeek theory
BJH	Barret–Joyner–Halender
RSM	Response surface method
M	Molarity
rpm	Revolutions per minute
BJH	Barret–Joyner–Halender
MCM	Meso- porous Silicate
FESEM	Field Emission Scanning Electron Microscopy
h-REFeO <sub>3</sub>	Hexagonal Rare- earth- iron oxides

## **PUBLICATIONS**

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6. Bronze Medal in CITREX Exhibition 2013, University of Malaysia Pahang.
7. Paper accepted in conference ICMEE, 2013 Yokohama, Japan.
8. Paper accepted in Nano Today 2013 Conference, Singapore, will be held in December 2013.

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## **PATENT APPLIED:**

Synthesis of Vanadium (III) doped cubic ferrite (magnetic nanoparticle).

Associate Prof. Dr. Abdurahman.H.Nour, Syed Farhan Hasany, and Prof. Dr. Jose Rajan.

## **CHAPTER I**

### **INTRODUCTION**

#### **1.1 INTRODUCTION**

This thesis presents the results of an experimental study of physical properties of vanadium tailored maghemite nanoparticles and noncovalent nanohybrids of maghemite – multiwalled carbon nanotubes (MWCNTs), that are synthesized by crystallization of amorphous precursors. In addition to the synthesis, maghemite – MWCNTs nanohybrids were employed in environmental study for the efficient removal of Lead (Pb II), from aqueous solutions. A mathematical model has been studied for the optimization of Lead removal efficacy from aqueous solutions.

Magnetic nano materials are highly pursued during the last two decades because of their improved thermo-physical properties in diverse engineering applications globally (Alivisatos, 1996; Fendler, 1998; Mahmoudi et al., 2011; Schmid, 1994; and Weller, 1993). The manipulation of matter, with control at nanometer dimensions, produces new structures, materials, and devices. Nano-particles promise an unprecedented advancement in many sectors, such as medicine, energy, materials, consumer products, and manufacturing (Tari et al., 1979; Poizot et al., 2000 and Mahmoudi et al., 2010). The main areas of application to date are in electronics, photonics, pharmaceuticals, chemical synthesis and analysis, cosmetics and finishes for surfaces and textiles. The synthesis of discrete magnetic nanoparticles with sizes ranging from 2 to 20 nm is of significant importance, because of their applications in magnetic storage devices (Awschalom and DiVincenzo, 1995; Billas et al., 1994; Handley et al., 1999 and Raj and Moskowitz, 1990). The unique magnetic property of the nano-particles arises mainly due to the reduced sizes of isolated nano particles and contributions from inter particle interactions are

negligible. The surfactant coating on magnetic nanoparticles prevents clustering due to steric repulsion. Dynamic adsorption and desorption of surfactant molecules on to particle surfaces during synthesis enable reactive species to be added onto the growing particles. These nanoparticles can be dispersed in many organic solvents and can be retrieved in powdered form by removing the solvent.

The preparation method plays a key role in determining the particle size and shape, size distribution, surface chemistry and therefore the applications of the material (Jeong et al., 2007). The conditions necessary for the formation of magnetic particles are essentially the same as for non-magnetic particles but some special precautions are necessary because of strong magnetic interactions among the particles. The essential parameters are:

- Separation of the nucleation process from the growing process.
- Protection of particles from aggregation.
- A controlled supply of precursor materials, and
- Temperature and pH of the solution.

## **1.2 PROBLEM STATEMENT**

Chemical synthesis and in particular, methods from organometallic Chemicals have been widely used to produce nanomaterials. (Klabunde et al., 1998) studied used Borohydride derivatives reduction methods extensively for the synthesis. The drawback of these reductions methods is the incorporation of boron in to the particles which leads to the modification of magnetic properties of the particles. Reduction of metal carbonyls studied by (Suslick et al., 1999) was not able to synthesis size and shape controlled nanomaterials.

(Dassenoy et al., 2000) studied the Hydrocarbyl complexes, by hydrogenating organometallic complexes containing an olefinic and poly olefinic ligand decomposed to give

bare metal atom which would condense in the reaction medium. Thus the particles are superparamagnetic with blocking temperatures near 10 K and display an enhanced magnetization at saturation per cobalt atom compared to bulk cobalt. Additions of O<sub>2</sub>, pyridine, isocyanides or CO lead to a dramatic decrease of the magnetic properties of the particles. This demonstrates that:

- The absence or low contamination of the as prepared particles, and
- The presence of a relation between the  $\pi$ -accepting properties of the ligand and the magnetic properties of the nanomaterials.

In general, the particle sizes, magnetic properties of magnetic nanoparticles can be controlled by systematically adjusting the reaction parameters, such as time, temperature, and the concentrations of reagents and stabilizing surfactants. Particle size increases with increasing reaction time, because more monomeric species are generated and with increasing reaction temperature because the rate of reaction is increased.

The following key issues for magnetic nanoparticle synthesis are problem statement of this research proposal.

- To study the particle size distribution (uniformity), in the synthesized mono dispersed magnetic nano particles.
- To study the particle size control of magnetic nanoparticles in a reproducible manner.
- To study the crystallinity and desired crystal structure of magnetic nanoparticles with satisfactory level of crystalline identity.
- To study the Shape-controlled synthesis of anisotropic nanoparticles in relation to specific applications.